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**The Vibrational Deactivation of HF($v = 3$) and
HF($v = 2$) by H Atoms**

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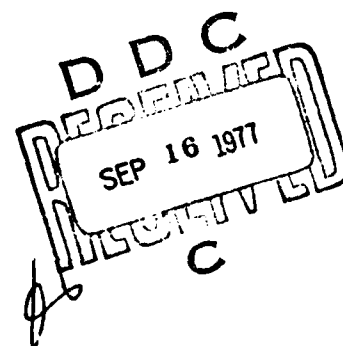
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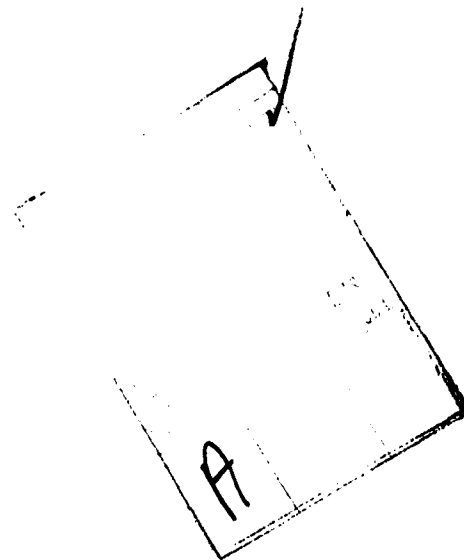
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The exponential decay times of the HF 3-0 fluorescence with and without the microwave discharge and the measured H-atom concentrations were used to calculate a removal rate of $6.3 \times 10^{13} \text{ cm}^3/\text{mol-sec}$ for HF($v = 3$). This rate is ~ 400 times faster than the deactivation of HF($v = 1$) by H atoms and ~ 100 times faster than the deactivation of HF($v = 2$) also reported in this study. Thus, it may account for the low laser output from the higher vibrational levels that has been observed in pulsed HF lasers.

There are several vibrational deactivation processes and reactions that may contribute to the measured removal rate. The present results bear directly on the construction of potential energy surfaces used for theoretical predictions of upper level deactivation rates.

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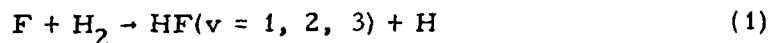
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I. INTRODUCTION

The interest in understanding and modeling the HF chemical laser has resulted in several theoretical^{1,2} and experimental³⁻⁵ studies of the deactivation of HF($v = 1$) by H atoms. The cold-reaction HF laser operates on the reaction in which one H atom is produced for each HF molecule. Therefore,



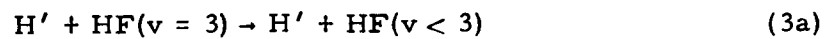
the importance of the HF(v) deactivation by H atoms must be evaluated relative to HF self-deactivation rates. The discrepancy between two of the experimental H + HF($v = 1$) studies^{4,5} and the classical trajectory calculations^{1,2} has stimulated interest in a more accurate determination⁶⁻⁸ of the potential energy surfaces that are required as input to the trajectory calculations of the deactivation rates. In addition to the vibrational deactivation measurements, studies^{5,9} of the reactions (2a) and (2b) resulted in upper limits for the rate of



F-atom exchange in Reaction (2b). These data may also be compared with theoretical predictions that are based on various potential energy surfaces.

In a previous study,⁵ the laser-induced fluorescence technique was used for measuring the room-temperature deactivation rate of HF($v = 1$) by H atoms. The study has been extended to include the H-atom deactivation rates of HF($v = 3$) and HF($v = 2$). The $v = 2, 3$ levels of HF are produced by sequential absorption of photons from the 1-0, 2-1, and 3-2 transitions of a pulsed HF chemical laser. The sequential photon absorption technique was used previously to study HF(v) deactivation by HF¹⁰ and other diatomic molecules¹¹ as well as V-V transfer from DF($v = 2$) to CO₂.¹² Isothermal calorimetry was used for the H-atom concentration measurements.⁵

The deactivation of HF($v = 3$) by H atoms can proceed by three channels:



nonreactive deactivation (3a), reactive deactivation by H-atom exchange (3b), and (3c) the back reaction of Reaction (1) to form H_2 . The channel represented by (3c) only becomes available for HF($v \geq 3$).

II. EXPERIMENTAL APPARATUS AND PROCEDURE

A. FLOW SYSTEM

The experimental apparatus used in this study is shown in Fig. 1. The fluorescence cell was slightly modified from the design of Ref. 5 and was constructed of 44-mm i.d. Pyrex tubing. The walls were coated with Halo-carbon wax in order to reduce H-atom recombination and loss of HF at the walls.⁵ Hydrogen atoms were produced by a 2450-MHz microwave discharge (≤ 50 W) in He-H₂ mixtures flowing through a quartz discharge tube of 10-mm i.d. and 20-cm length. This discharge tube was connected to the main flow tube approximately 7 cm upstream of the region where the laser-induced fluorescence was monitored. A mixture of 10% HF in helium was injected into the gas stream approximately 5 cm upstream of the fluorescence window in order to permit ~ 20 msec for mixing in the 300 cm/sec flow. The mass flows were measured with rotating ball flowmeters calibrated by pressure-rise measurements in a standard volume.

B. LASER-INDUCED FLUORESCENCE

The laser used to pump HF($v = 2, 3$) has been described in previous studies.^{11, 13} It could be pressure-tuned such that HF($v = 1, 2$) only or HF($v = 3$) as well were produced in the fluorescence cell. The fluorescence region was focused onto a photomultiplier with an f/1.5 quartz lens system. An RCA 7102 photomultiplier (S-1) was used for the $v = 2$ experiments. A silicon flat in front of the photomultiplier restricted the monitored fluorescence to wavelengths $> 1 \mu\text{m}$. An RCA C-31034 (GaAs) photomultiplier was used for the $v = 3$ experiments; a narrow band filter restricted the fluorescence to a 200 Å spectral band centered at 8900 Å. The output signal across a 47 KΩ resistor was amplified by a Perry Model 070 amplifier (15 × amplification) and recorded with a Biomation 805 transient recorder. The recorded signals were transferred to a Nicolet Model 1072 signal averager, where 128 to 512 experiments were typically stored and averaged before being displayed on an X-Y recorder.

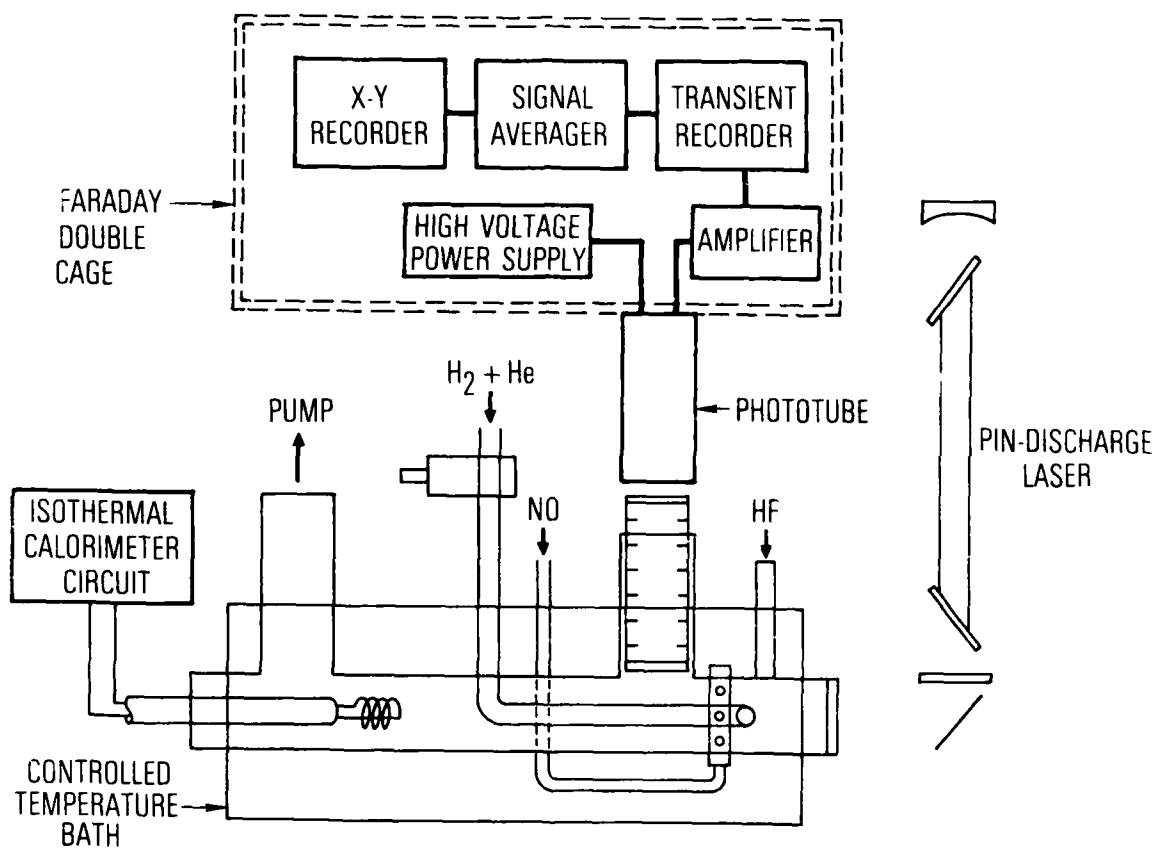


Figure 1. Schematic of Apparatus

C. ISOTHERMAL CALORIMETER

The construction, operation, and calibration of the isothermal probe has been described previously.⁵ The heated Pt-wire coil recombined H atoms in the present 44-mm-i.d. fluorescence cell with an efficiency of $\sim 70 \pm 10\%$, which was slightly less than its efficiency in the 22-mm-i.d. tube of the previous experiment.⁵

D. MATERIALS

HF (Matheson Co., 99% liquid phase) was purified by pumping on samples at 77 K in order to remove the noncondensibles and then distilled into a passivated 4 liter stainless-steel tank. The HF was diluted 1:10 in He to a total sample pressure of 2 to 3 atm absolute. Helium (Air Products 99.995%) was passed through a molecular sieve trap that was periodically baked out under vacuum at elevated temperature. Hydrogen (Matheson, 99.95%) was also passed through a molecular sieve for the $v = 3$ and some of the $v = 2$ experiments. In some of the $v = 2$ experiments, the H_2 at 1 atm was passed over $H_2O(S)$ at $-35^\circ C$ in order to increase the H-atom production.

III. RESULTS

Experiments were performed at 2.6 to 3.9 Torr total pressure with partial pressures of 0.02 to 0.08 Torr for H_2 , 0.003 to 0.018 Torr for H atoms, and 0.0005 to 0.002 Torr for HF with the balance consisting of He. The measured fluorescence traces were plotted on semilog paper, and exponential decay times τ were determined. In each experiment, the decay times were measured with the microwave discharge on (τ_{on}) and with the discharge off (τ_{off}) while the other conditions were kept constant. The measured decay times and the experimental conditions are given in Tables I and II. The decay times are described by

$$\tau_{off}^{-1} = k_{HF-H_2} [H_2]^{\circ} + R_{off} \quad (4)$$

$$\tau_{on}^{-1} = k_{HF-H_2} ([H_2]^{\circ} - 1/2[H]) + k_{HF-H} [H] + R_{on} \quad (5)$$

$$\tau_{on}^{-1} - \tau_{off}^{-1} = (k_{HF-H} - 1/2k_{HF-H_2}) [H] + (R_{on} - R_{off}) \quad (6a)$$

where k_{HF-H} is the total removal rate of HF(v) by H atoms [Reactions (3a), (3b), and (3c)]; k_{HF-H_2} is the removal rate of HF(v) by H_2 ; R_{on} and R_{off} are the quenching rates for those processes (e.g., diffusion, convection) that do not involve H and H_2 ; and $[H_2]^{\circ}$ is the concentration of H_2 in the cell with the microwave discharge off. The values of $R_{on} - R_{off}$ were determined to be smaller than the uncertainties in the measured decay times for HF(v = 2) and were completely negligible in the HF(v = 3) experiments.

The values of $\Delta\tau^{-1} = \tau_{on}^{-1} - \tau_{off}^{-1}$ obtained in the HF(v = 3) experiments are plotted in Fig. 2 versus the concentration of H atoms. As shown in (6a)

Table I. Removal Rate of HF($v = 3$) by H Atoms

Run No.	P _{total} , Torr	(H) $\times 10^{10}$, mol/cm ³	(H ₂) $\times 10^9$, mol/cm ³	τ_{on} , μ sec	τ_{off} , μ sec	$\Delta(1/\tau) \times 10^{-4}$, sec ⁻¹
1	2.65	3.2	4.0	28.7	215	3.0 ± 0.22
2	2.65	2.4	4.0	37.4	215	2.2 ± 0.1
3	2.65	4.3	4.0	25.6	177	3.4 ± 0.2
4	2.6	5.6	1.8	21.8	270	4.2 ± 0.2
5	2.5	5.6	1.8	22.4	270	4.1 ± 0.2
6.	2.65	5.6	1.83	22.0	270	4.2 ± 0.2
7	2.65	7.7	1.83	14.1	270	6.7 ± 0.4
8	2.65	2.2	1.83	26.2	260	3.4 ± 0.2
9	2.65	2.0	1.83	30.7	260	2.9 ± 0.2

Table II. Removal Rate of HF($v = 2$) by H Atoms

Run No.	P _{total} , Torr	(H) $\times 10^{10}$, mol/cm ³	(H ₂) $\times 10^{10}$, mol/cm ³	τ_{on} , μsec	τ_{off} , μsec	$\Delta(1/\tau)$, sec ⁻¹
1	2.8	9.6	28	121	128	400
2	2.8	9.6	28	113	124	730
3	2.8	7.6	21	161	153	-120
4	2.8	8.6	21	148	172	970
5	2.8	8.2	28	141	150	440

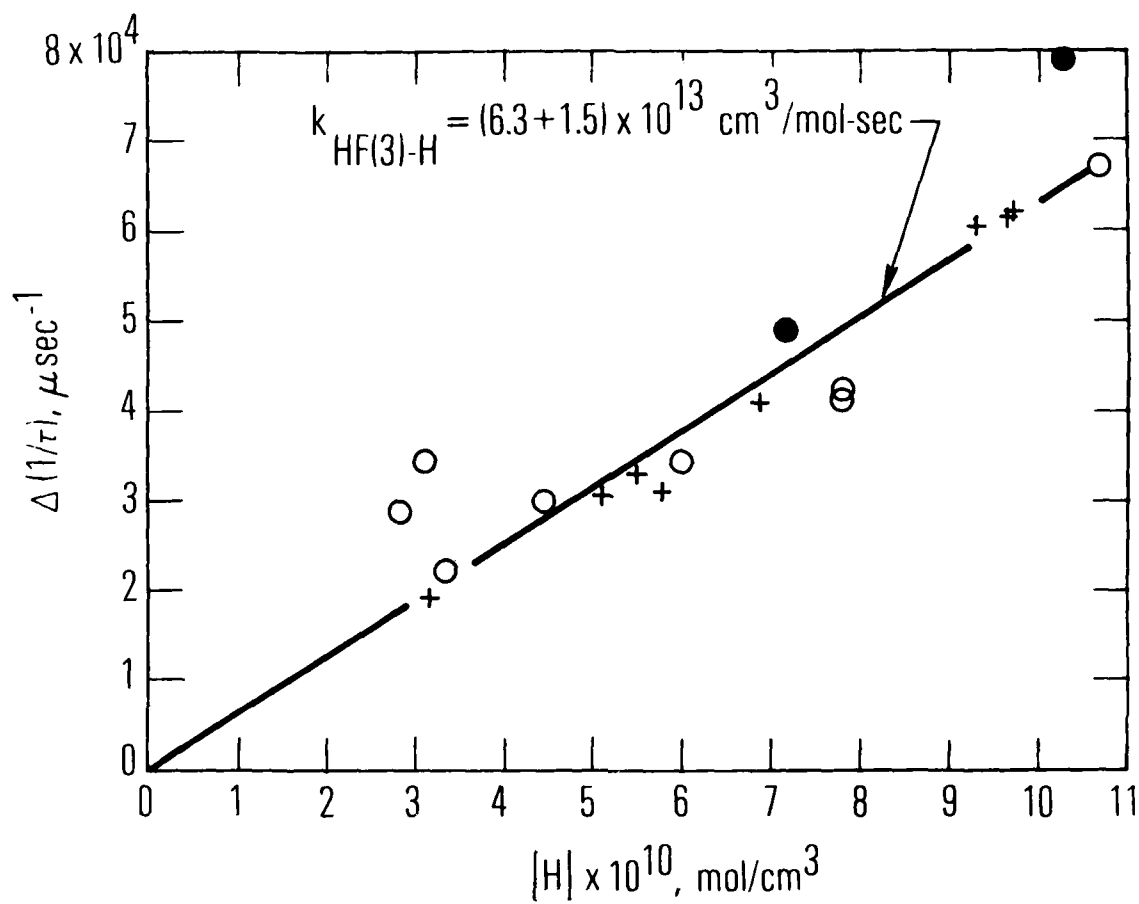


Figure 2. Removal Rates of HF($v = 3$) by H Atoms. Symbols represent three sets of experimental data.

the slope of the data is proportional to $(k_{\text{HF-H}} - 1/2 k_{\text{HF-H}_2})$ and has a value of $(6.3 \pm 1.5) \times 10^{13} \text{ cm}^3/\text{mol-sec}$. The quoted error reflects the systematic uncertainties in the calibrations of the isothermal probe and flowmeters as well as those due to the experimental scatter. Since $k_{\text{HF-H}_2}$ for $\text{HF}(v = 3)$ has been measured¹¹ to be $2.1 \times 10^{11} \text{ cm}^3/\text{mol-sec}$, it is negligible compared with the slope and, therefore, with the value of $k_{\text{HF-H}}$. If Reaction (3c) completely dominates over (3a) and (3b), there is a small reduction in the apparent decay of $\text{HF}(3)$ because of the back reaction of $\text{F} + \text{H}_2$. After the rapid equilibrium of F atoms is established, it can be shown that the measured decay rate would be

$$\tau_{\text{on}}^{-1} - \tau_{\text{off}}^{-1} = \left(k_{3c} \left[\frac{k_1 - k_{3c}}{k_1} \right] \right) [\text{H}] \quad (6b)$$

where $(k_1 - k_{3c})/k_1$ has been determined¹⁴ to be 0.72. These theories will be expanded in a subsequent paper.¹⁵

In the experiments in which the $\text{HF}(v = 3)$ removal rate was measured, τ_{on} was 5 to 20 times smaller than τ_{off} . In those in which the $\text{HF}(v = 2)$ removal rate was measured, τ_{on} was only slightly shorter than τ_{off} at approximately the same H-atom concentrations used for the $\text{HF}(v = 3)$ experiments. These latter data were obtained with the laser detuned such that $\text{HF}(v = 1, 2)$ only were directly pumped by the laser. This prevented cascading effects from $\text{HF}(v = 3)$. The data for $v = 2$ are presented in Fig. 3 and indicate a value of $(5.5 \pm 3) \times 10^{11} \text{ cm}^3/\text{mol-sec}$ for $k_{\text{HF-H}} - 1/2 k_{\text{HF-H}_2}$. Using the value of $2.26 \times 10^{11} \text{ cm}^3/\text{mol-sec}$ ¹¹ for $k_{\text{HF-H}_2}$, the removal rate of $\text{HF}(v = 2)$ by H_2 , we obtained a value of $(6.6 \pm 3) \times 10^{11} \text{ cm}^3/\text{mol-sec}$. Because of the fairly small differences between τ_{on} and τ_{off} , there was more scatter in the values of $\Delta(1/\tau)$ for the $\text{HF}(v = 2)$ than for the $\text{HF}(v = 3)$ measurements.

In any study of upper level deactivation, the V-V exchanges between the various vibrational levels must be carefully considered because they can

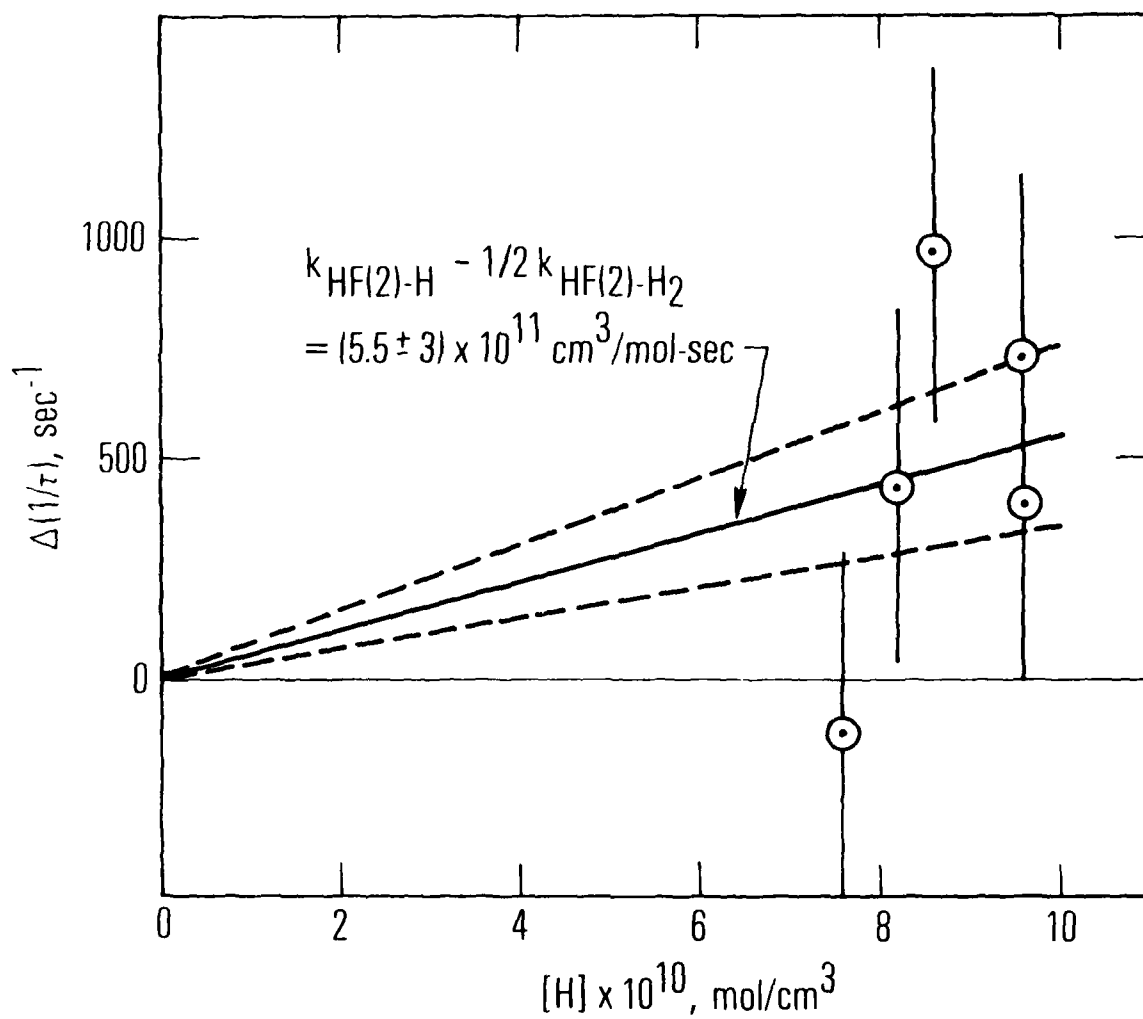
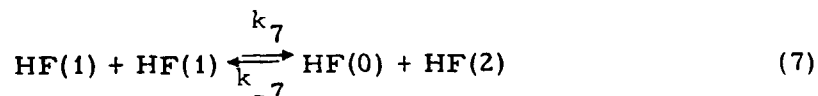


Figure 3. Removal Rates of HF($v = 2$) by H Atoms

act to deplete a given level or to pump it. The primary V-V process that affects HF(v = 2) is the exchange



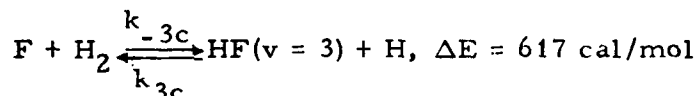
which can be included in R in Eqs. (4) and (5) as

$$R^{VV} = k_7 [\text{HF}(1)]^2 / [\text{HF}(2)] - k_{-7} [\text{HF}(0)] \quad (8)$$

The removal term $-k_{-7}[\text{HF}(0)]$ applies with or without H atoms and, therefore, cancels in (6a). The pumping term $k_7[\text{HF}(1)]^2 / [\text{HF}(2)]$ also cancels near time equal to zero as the initial concentrations of HF(2) and HF(1) were not affected by the presence of the H atoms.¹¹ More importantly, if the pumping term were significant, the fluorescence traces would not decay exponentially with time. The traces decayed exponentially for the first 1 to 2 decay times.

IV. DISCUSSION

The removal rates for HF($v = 2$) and HF($v = 3$) obtained in this study are given in Table III together with that for HF($v = 1$) obtained in a previous study.⁵ HF¹⁶⁻¹⁸ self-relaxation rates are also given for comparison. Although there is a large uncertainty in the rate for HF($v = 2$) removal by H, the rate appears to be ~ 4 times faster than the comparable process involving $v = 1$. By contrast, the removal of HF($v = 3$) by H atoms is faster by a factor of 100 than that for HF($v = 2$). One of the three possible processes for HF($v = 3$) removal is Reaction (3c), which, in the backward direction, is a component of Reaction (1). In their review of the rate measurements for Reaction (1), Cohen and Bott¹⁴ recommended a room-temperature value of 1.5×10^{13} cm³/mol-sec and an initial distribution over the vibrational levels such that the rate



k_{-3c} was 4.2×10^{12} cm³/mol-sec. The values of k_{3c} and k_{-3c} can be related by the principle of detailed balance. This should be a good approximation inasmuch as Reaction (-3c) is endothermic by only 617 cal/mol, or ~ 1 kT. By using the principle of detailed balance, a value of 1.4×10^{13} cm³/mol-sec can be calculated for (3c). Although this rate is a factor of 4.5 smaller than the removal rate measured in this study, the calculated value for k_{3c} is somewhat uncertain. An uncertainty of 180 cal/mol in the spectroscopically determined bond-dissociation energy of HF^{19,20} produces an uncertainty of a factor of 1.4 in the equilibrium constant for (3c) at 295 K and, therefore, in the calculated value of k_{3c} . Another factor of 1.5 uncertainty must be considered possible for the overall F + H₂ rate and the fraction of this

Table III. Removal Rates of HF(v) by H Atoms at T = 295 K
Compared with HF(v) V-R, T Relaxation by HF

v	HF(v)-H		HF(v)-HF	
	$^3k(v)$, cm ³ /mol-sec	Ref.	$^3k(v)$, cm ³ /mol-sec	Ref.
1	^a (1.4 ± 0.4) × 10 ¹¹	5	1.1 × 10 ¹²	16
2	(6.6 ± 3) × 10 ¹¹	This study	6 × 10 ¹²	17
3	(6.3 ± 1.5) × 10 ¹³	This study	1.3 × 10 ¹³	18

^aQuigley and Wolga⁴ reported a smaller value as an upper limit to this rate.

reaction that goes into HF($v = 3$).¹⁴ Therefore, k_{FC} could be as large as $3 \times 10^{13} \text{ cm}^3/\text{mol-sec}$.

The other two possible contributors to the measured removal rate of HF($v = 3$) are channels (3a), nonreactive and (3b), reactive deactivation. The nonreactive deactivation rates of HF(v) by H atoms can be expected to increase with v . The results of trajectory calculations^{1,2} indicate that the rates may increase by a factor of ~ 3 from $v = 1$ to $v = 2$ and ~ 2 to 3 from $v = 2$ to $v = 3$. These increases are consistent with the present results for HF($v = 1$) and HF($v = 2$) removal rates but can not explain the fast HF($v = 3$) rate.

Wilkins²¹ performed trajectory calculations for H + HF($v = 3$) removal by H atoms on London-Eyring-Polanyi-Sato (LEPS) potential-energy surfaces designed to have barriers of 1.5, 2.5, and 40 kcal/mole for the exchange reaction



The results of these calculations are given in Table IV. For the low barriers, the deactivation occurred by both reactive and nonreactive collisions (3a) and (3b). The deactivation occurred solely by nonreactive collisions in the calculations with the 40 kcal/mol barrier. All of the calculated rates are slower than the measured value.

Recently, a priori quantum mechanical calculations were performed by Bender and co-workers⁶ on the H + FH potential energy surface. They calculated a barrier height of 49 kcal/mole for the exchange reaction (9), but estimated that it might be as low as 40 kcal/mole. Preliminary results of similar calculations by Wadt and Winter^{7,8} also indicate a high barrier (35-40 kcal/mol). They found that the angular dependence of the theoretical surface differed markedly from the LEPS potential-energy formulation. Experimental measurements of the removal rates of DF by H atoms⁹ have been interpreted as support for those quantum mechanical calculations. The $v = 3$ level of HF lies 38.3 kcal/mol above the bottom of the well and

Table IV. Calculated Deactivation Rates^a of HF($v = 3$) by
H Atoms at $T = 295\text{ K}$

Barrier Height, kcal/mol	k , $\text{cm}^3/\text{mol-sec}$	Ref.
1.5	1.4×10^{13}	2
2.5	1.6×10^{12}	21
40.0	2.5×10^{12}	21

^aThe calculated rate k represents the sum of k_{3a} and k_{3b} .

32.5 kcal/mol above $v = 0$; thus, $\text{HF}(v = 3)$ molecules have vibrational energy comparable to the estimates of the barrier.

In a classical trajectory calculation, Smith and Wood²² investigated the relaxation of vibrationally excited molecules in collisions where an atom exchange reaction is possible. In particular, they studied $\text{H} + \text{H}_2(v = 1, 2)$, $\text{Cl} + \text{HCl}(v = 1, 2)$ and $\text{H} + \text{ClH}(v = 1, 2)$ and found that the vibrational energy lowers the threshold and activation energy in the three cases, although the extent of the lowering depends on the particular mass combination. Collisions in which the energy barrier was crossed had a wide distribution of product vibrational energies, whereas those in which the barrier was not crossed were highly adiabatic. In some of the $\text{A} + \text{BC}$ collisions above the barrier, B was closer to A than C at one or more points in the trajectory even when the final products remained A and BC. Vibrational excitation of BC above the barrier not only permits atom exchange with consequent loss of vibrational energy but also permits these multiple interactions, which increase the possibility for conversion of vibrational energy to rotational or translational energy.

The difficulty of product determination in the present experiment is much greater than that of the measurement of the total removal rate of $\text{HF}(v = 3)$. The present results do not establish the contribution of the three possible channels to the total rate. If the recommended rate for Reaction (1) is correct and the exothermicity of (3c) is ~ 617 cal/mole, then channel (3c) accounts for $\sim 1.4 \times 10^{13} \text{ cm}^3/\text{mol-sec}$, which leaves $\sim 5 \times 10^{13} \text{ cm}^3/\text{mol-sec}$ of the measured rate to be ascribed to channels (3a) and (3b). The trajectory calculations on LEPS surfaces do not account for so fast a rate. Clearly, more work is needed in order to establish the mechanism of the observed removal rate of $\text{HF}(v = 3)$ by H atoms.

In previous efforts to model pulsed laser performance,^{17,23-25} large deactivation rates for the upper vibrational levels had to be used. This upper-level deactivation can be due to HF or H or both. The removal rate of $\text{HF}(v = 3)$ by $\text{HF}(v = 0)$ obtained by Osgood and co-workers¹⁰ contains

contributions from both V-V and V-R, T processes. With a computer modeling study, Cohen and Bott¹⁷ concluded that the V-R, T rate for HF($v = 2$) deactivation by HF($v = 0$) is $\sim 6 \times 10^{12} \text{ cm}^3/\text{mol-sec}$, or six times that for HF($v = 1$). Chen and co-workers²⁴ found that their experimental results could be modeled with the HF-HF, V-R, T rates scaled to the upper vibrational levels as v^2 . Preliminary results obtained by Kwok¹⁶ indicate a $v^{2.3}$ dependence. Therefore, the HF($v = 3$) -HF V-R, T deactivation rate may be ~ 1 to $2 \times 10^{13} \text{ cm}^3/\text{mol-sec}$. This rate, although fast, is still slower than the results of the present study for the rate of HF(3) removal by H atoms (Table III). Since H atoms and HF are found in equal proportions in cold-reaction lasers, they may play a significant role in determining the amount of power observed from upper vibrational level laser transitions. The effect on chain-reaction lasers is less well-defined since it depends upon the initial F_2 dissociation.

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